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ELECTRODIC MEMBRANES SELECTIVE FOR Ag^+ AND THEIR APPLICATIONS IN VITAMIN CONTENT POTENTIOMETRIC DETERMINATION

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Se prezintă în această lucrare caracteristicile unui electrod ion-selectiv pentru ionul de Ag^+, obtniut prin inglobarea in membrana electrodică a unui compus organic derivat de dodecil tetratio 14-coroana-4 drept receptor. Urmatoarele influente asupra raspunsului electrodului au fost studiate: variația pH-ului, tipul de plastifiant şi compozitia electrolitului intern. Au fost de asemeni determinate valorile coeficientilor de selectivitate. Electrodul obtinut a fost aplicat în determinarea vitaminei B1 din tablete farmaceutice.

The characteristics of a new Ag+-ion selective electrode obtained using dodecyl tetrathio 14-crown-4 derivative as ionic receptor, in electrodic membranes are presented. There were studied several influences like: pH, plasticizer, composition of internal electrolyte on the response of the potentiometric sensor. Selectivity coefficients as well as its application in vitamin B1determination are presented.

Keywords: ion selective electrode, thioethers, Ag^+

1. Introduction

In the recent years, the design of carrier-based Ag^+- ion-selective electrodes (ISEs) has gained importance, mainly due to the neutral ionophore-based Ag^+-ISEs, which are better from the point of view of characterization than standard Ag_2S-based solid state electrodes [1].

[3] The development of membrane ion - selective electrodes is one of the most important areas of research using macrocyclic compounds in electroanalytical chemistry [1]. In literature there are presented several studies and examples of ISEs for cations, anions and neutral species, fully characterized and used in environmental and clinical applications [2,3].

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The polivalent nature of silver makes its analysis in and recovery from several kinds of samples of great importance [4].

Many podands, crown ethers and calixarenes derivatives have been used in polymeric membranes, because of their ability of forming complexes with metal ions of compatible dimensions, as ionophores for the determination of Ag^+ [5].

Polythioethers have been firstly entrapped in electrodic membranes twenty years ago. Kamata[6] designed a copper(II) electrode using as active compound 13,14-benzo-1,4,8,11-tetrathiocyclopentadecane. Lai [7] presented ISE for $Ag^+$and Hg^{2+} with dithio 15-crown-5 entrapped in the membrane. These electrodes did not present a Nernstian response for Ag^+ (the slope value - 40 mV/decade). For Hg^{2+}, the slope had a a Nernstian value in the range 10^{-6}- 10^{-3} M. Brzozka [8] used different coronands, cryptands or podands containing sulphur atoms as ionophores in the polymeric membrane The selectivity of these sensors depends on the type of ionophore, these membranes being selective for Cu^{2+}, Cd^{2+}, Hg^{2+}, Ag^{2+} and Pb^{2+}.

In further studies, there have been used, in order to avoid the leaching out of the membrane more lipophilic compounds [9,10]. Pretsch [11,12] studied the posibility of obtaining lower detection limits of ion selective polymeric membrane electrodes (ISE) for Pb^{2+}, Ag^+ and Ca^{2+} by using certain internal electrolytes. Polythiamacrocycles, bis-pyridine tetramide macrocycle, bis(dialkyldithiophosphate)derivative and o,o,o-trialkyl phosphorothioates have been reported as effective ionophores to build Ag^+ selective electrodes[13 – 16].

By using ionophores containing sulfur and nitrogen atoms in ion-selective electrodes, it is expected that the electrodes are sensitive to soft heavy metal ions [17,18].

The preliminary results obtained in using dodecil tetrathio 14-crown-4 derivative as ionic receptor for Ag^+ selective electrode concerning: the response, selectivity coefficients, influence of the plasticizer, the pH and the influence of the composition of the internal electrolyte over the detection limit are presented. This ligand not very difficult to synthesize, with four donor sulfur atoms are expected to form selective complexes with transition-metal ions and to give an improved selectivity for the silver ions.

2. Experimental

For all experiments doubly distilled water and chemicals of pa grade were used.

Standard solutions (0.1 M) of metal salts were prepared from nitrates salts of Zn^{2+}, K^+, Cu^{2+}, Cd^{2+} and Pb^{2+}. Working solutions were prepared as required by suitable dilution with doubly distilled water. The pH of the solutions was adjusted with 0.1 M nitric acid.

The solvent polymeric membranes were prepared according to [8] by using 1 wt % carrier, 66wt % plasticizer and 33 wt % poly(vinylchloride) (PVC high molecular; purum pa, Fluka AG). As lipophilic anionic sites, 50 mol % potassium tetrakis(p-chlorophenyl)borate(KTpClPB; purum pa Fluka) taking into account the ionophore was incorporated. Plasticizers used in this work:

o-nitrophenyl octyl ether(o-NPOE; puriss pa, Fluka); dioctyl sebacate(DOS; puriss pa Fluka); dioctyl phtalate (DOP; puriss pa Fluka) and trioctyl phosphate (TOP; puriss pa Fluka). The membrane components were dissolved in 2 ml freshly distilled THF. This solution was cast into 24 mm i.d. glass rings resting on a glass plate. After the overnight solvent evaporation, the resulting membrane was peeled from the glass mould and disks of 7 mm diameter were mounted in miniaturised electrode bodies (handly made) for performing e.m.f . measurements.

E.m.f. measurements were carried out at 20^0 C with cells of the type: Hg, Hg_2Cl_2: KCl(satd)/1 M KNO_3/sample//membrane//internal filling solution: AgCl;Ag. The $AgNO_3$ solutions at fixed pH and 1 ml 0.1 M $AgNO_3$ in 100 ml 0.05 M EDTA-Na_2 at fixed pH were used as internal electrolytes

Potentials were determined using an Elit interface 8801 pH-meter. The data acquisition was performed as in [17].

The selectivity coefficients $k^{pot}_{Ag,M}$ were calculated using the fixed interference method [19] by measuring the e.m.f of silver(I) solutions in the pAg range of 1-6 with the conventional internal electrolyte and of 1-9 with the new one with a constant concentration of interfering cation (10^{-2} M). Selectivity coefficients were also determined by the separate solution method [19] using 10^{-2} M solutions of the metal nitrates at a constant pH.

The content assay of vitamin B1 in tablets was found according to the following procedure: About 1 g of vitamin B tablet finely powdered was dissolved in 100 mL distilled water. 10 mL of the resulting solution was transferred to a 25 mL beaker and both the silver electrode the reference electrode were immersed in it. The solution was titrated with a 5.00x10-2 M AgNO3 solution. The end-point of the titration was potentiometric determined.

3. Results and discussion

The electrode was characterized and tested for a variety of cations (K^+, Zn^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+}) in preliminary experiments.

Response of the electrode and the calibration range

Electrodes with membranes containing dodecil tetrathio 14-crown-4 derivative were prepared and the response was tested in membranes with 50 %mole (vs. ionophore) KTpClPB without lipophilic salts and with two different internal electrolytes. These electrodes were kept in double distilled water for two days before the measurements. The remarkable difference in the response of the electrodes proves that an increased lipophilicity of the ionophore avoids its leaching out of the membrane, Table 1. The response time is about 30 seconds.

With the conventional inner filling solution, the detection limit for Ag^+ is about –5.5 M. Using the new internal electrolyte, leaching out of the primary ion from the membrane was prevented by building up a concentration gradient into the membrane. This concentration gradient is established by choosing an internal electrolyte with low activity of the primary ion.

The responses of the Ag^+ ISE with the same membrane but different inner reference systems are presented in fig.1. With the conventional inner filling solutions, the linear near Nernstian response range for Ag^+ is extended to about 10^{-9} M and the detection limit to –7.5 M in comparison with –5.5 M using the conventional electrolyte.

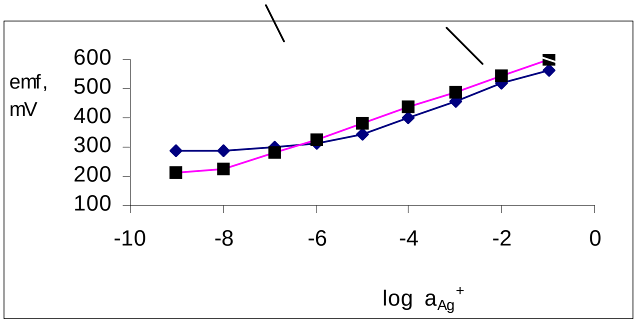

Fig.1. The response of Ag^+ ISEs with the same membrane but two internal electrolytes; (▲)0.1 M $AgNO_3$ solution at pH = 4.52. (■) 1 ml 0.1 M $AgNO_3$ in 100 ml 0.05 M EDTA-Na_2 at pH = 4.5

Selectivity

Selectivity coefficients values presented in Table 1 were also improved using the buffered electrolyte. It can be seen that most values are lower using the new buffered internal electrolyte, which confirms the corresponding shift of the lower detection limit.

Table 1

Logarithmic values of the selectivity coefficients log $K^{pot}_{Ag, M}$ with two different internal electrolytes

Ion M	$\log K^{pot}_{Ag^+, M}$	
	Conventional electrolyte	Buffered electrolyte
K^+	-4.5	-6.4
Zn^{2+}	-3.7	-5.0
Cu^{2+}	-2.7	-4.4
Cd^{2+}	-2.5	-4.1
Pb^{2+}	-1.5	-2.0

The alcaline metal cations present a negligible influence on the selectivity. In comparison with the Ag$^+$ ISE with Ag_2S solid membrane, the electrode with liquid membrane having dodecil tetrathio 14-crown-4 derivative entrapped in the membrane presents superior values of selectivity coefficients (Table 1).

Influence of membrane composition on the characteristics of the electrode

The influence of the plasticizer in the membrane was studied. More polar the plasticizer is, better values in terms of selectivity coefficients are obtained. Selectivity coefficients for membranes with different plasticizers are given in Table 2. It could be observed that best values are generally obtained when using o-NPOE. However, for bigger Ag$^+$ concentrations, the sensibility of the electrode is not satisfactory.

Table 2

Selectivity coefficient values for several plasticizers used in the membranes

Interferent	$\log K^{pot}_{Ag^+, M}$			
	DOS	DOP	o-NPOE	TOP
K^+	-3.8	-3.5	-4.5	-3.5
Zn^{2+}	-2.9	-2. 5	-3.7	-2.5
Cu^{2+}	-2.0	-2.0	-2.7	-2.0
Cd^{2+}	-2.9	-2.5	-2.5	-3.0
Pb^{2+}	-1.0	-1.0	-1.5	-1.1

Influence of pH on the response of the electrode

Influence of pH on the response of this electrode was studied. pH values were adjusted with nitric acid or sodium hydroxide. pH values over 7.5 lower e.m.f values due to Ag_2O precipitation. pH values under 2 lower e.m.f. values too, due to tetrathio ether protonation and subsequently reduce its capacity of complexation. All measurements were performed at an optimum pH value of 4.5.

Analytical application

Vitamin B1 is a chloride salt which has two Cl^- ions in the molecule. The vitamin B1 content in pharmaceutical tablets is potentiometric determined, the equivalence point being graphically determined. The results were compared with those obtained using the conventional titration method using $AgNO_3$ as titration reagent and $K_2Cr_2O_7$ as an indicator. The results are presented in Table 3.

Table 3

Determination of the content of Vitamin B1 (*a) and the standard deviations (*b) by the methods in pharmaceutical tablets

Sample	Ag+ ISE % s.d. (n=5)	Conventional titration % s.d. (n=5)
1	12.25/0.08	12.40/0.05
2	12.32/0.06	12.35/0.05
3	12.40/0.05	12.40/0.05
4	12.35/0.06	12.40/0.05

*a expressed in % (mass)
*b standard deviations for five measurements

4. **Conclusions**

PVC membranes electrodes incorporating dodecil tetrathio 14-crown-4 derivative show high selectivity and sensitivity towards silver ions. This electrode displays vry good selectivity for Ag^+ with respect to alkali, alkaline earth and common transition metal ions. It shows sufficiently low response towards Hg^{2+} which is a major interfering ion in Ag+ potentiometric determinations.

The advantages of this electrode are: reduced influence of Hg^{2+} as interferent in the sample solution; large range of pH between 2 and 7 in which this sensor could be used; significant increase of silver selectivity in samples with complex matrix.

The new composition found for the internal electrolyte allows ISE to be applied in modern trace electroanalytical determinations in environmental and clinical analysis.

This electrode was employed as an indicator electrode in potentiometric titrations of the vitamin B1 with convenient results.

R E F E R E N C E S

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